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PARTICLE-SIZE DISTRIBUTIONS IN BROWNIAN MOTION

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The Pioneering Research Laboratory on Physics of Fine Particles was established in 1962, at the Ohio Agricultural Experiment Station, Wooster, by the Agricultural Research Service of the United States Department of Agriculture, in recognition of the need for continued fundamental research on fine particle behavior and, in particular, the criticality of such studies to agriculture.

In agriculture, pesticides in both liquid droplet and solid particle form are used extensively, but their use is frequently hampered by lack of optimum efficiency and precision of application, despite the best efforts of manufacturers and applicators. This results in an excessive economic burden on agriculture in the maintenance of the best of quality in agricultural produce, as well as an increased chance of contaminating surrounding areas. Problems of air pollution are also of prime pertinence and concern. It is desired that the results of these investigations in fine particle behavior and its inherent subject matter will serve agriculture and its allied industries, and other industries with similar vexations, in the alleviation of these problems.

PARTICLE-SIZE DISTRIBUTIONS IN BROWNIAN MOTION

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A method of incorporating a particle-size distribution into statistical treatments of Brownian motion theory is considered. Probabilistic statements for the joint distribution of position and particle-size and conditional distributions of position on particle-size and particle-size on position, as functions of time are developed. Chandrasekhar's problem on the effect of Brownian motion on gravity sedimentation is used as an illustration for determination of a joint distribution.

INTRODUCTION

The applications of probability theory to the dynamics of Brownian motion are familiar. In this note we will consider a method of expressing the existence of a particle-size distribution in such problems. For a thorough discussion of the probabilistic concepts and notation used in this paper, the reader will find Feller [2] and Cramér [3] (*pp. 267–70, 291*–92) helpful.

PRELIMINARY CONSIDERATIONS

First imagine that we have N particles which may be put into n discrete classes of characteristic size $s_j (j=1, 2, \ldots, n)$ with N_j particles in s_j. The particles are then subjected to an unspecified process in time which continually rearranges them among M cells. Each of the p cells is assigned an identification number $i=1, 2, \ldots, M$, and we specify that the total number of particles shall remain constant.

At time t, we stop the process and perform an accounting of the particle arrangement. We count the total number N_i of particles of all sizes in cell i. The number N_{ij} of particles of size s_j in cell i is then counted. This will give the necessary information to estimate several probabilities which are required, since we could imagine the counts to be arithmetic mean values of several trials.

The probability of finding any particles in cell i, at time t, irrespective of their size s_j will be

$$P\{i; t\} = \frac{N_i}{N} \cdot \tag{1}$$

The probability of finding, at time t, any particles of size s_j in cell i will be

$$P\{i, j; t\} = \frac{N_{ij}}{N} \cdot \tag{2}$$

The probability of finding any particles of size s_j in the entire system will be independent of time and given by the particle-size probability function

$$P\{j\} = \frac{N_j}{N} \cdot \tag{3}$$

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[1] Pioneering Research Laboratory on Physics of Fine Particles, Agricultural Engineering Research Division, ARS, USDA, Wooster, Ohio.

[2] W. Feller. An Introduction to Probability Theory and Its Applications. 2d ed., Vol. i, Chap. v. New York. 1957.

[3] H. Cramér. Mathematical Methods of Statistics. 575 pp. Princeton, N.J. 1946.

The conditional probability that a particle will be found in cell i at time t on the hypothesis that it is of size s_j will be given by

$$P\{i|j;t\}=\frac{N_{ij}}{N_j}=\frac{P\{i,j;t\}}{P\{j\}}. \tag{4}$$

The probability that a particle of size s_j will be found at time t on the condition that we search in cell i will be

$$P\{j|i;t\}=\frac{N_{ij}}{N_i}=\frac{P\{i,j;t\}}{P\{i;t\}}. \tag{5}$$

Eq. (5) is a statement of the particle-size distribution in space as a function of time.

In (1), (2), and (4), and (5) the variable t is not distributed, but the probabilities are functions of time.

THE DISCRETE CASE IN ORDINARY SPACE

The development is similar to that of the preceding section if the cells are replaced by M discrete regions in ordinary space. In this case, the location of each region is specified in terms of a position vector $\mathbf{r}_i$ with components of scalar magnitude r_{i1}, r_{i2}, and r_{i3}.

The conditional probability, at time t, of the event $\xi=\mathbf{r}_i$ relative to the hypothesis $\eta=s_j$ will be as in (4), viz.

$$\begin{aligned} P(\xi=\mathbf{r}_i|\eta=s_j;t)&=\frac{P(\xi=\mathbf{r}_i,\eta=s_j;t)}{P(\eta=s_j)} \\ &=\frac{p_{ij}}{p_{.j}}, \end{aligned} \tag{6}$$

where p_{ij} is the joint probability of the events $\xi=\mathbf{r}_i$ and $\eta=s_j$, and $p_{.j}$ is the marginal probability

$$p_{.j}=\sum_i^M p_{ij}. \tag{7}$$

The conditional probability, at time t, of the event $\eta=s_j$ on the hypothesis that $\xi=\mathbf{r}_i$ will be given by

$$P(\eta=s_j|\xi=\mathbf{r}_i;t)=\frac{P(\xi=\mathbf{r}_i,\eta=s_j;t)}{P(\xi=\mathbf{r}_i;t)} \tag{8}$$

as in (5). Since the events $\eta=s_j$ are mutually exclusive, we may write

$$\begin{aligned} P(\xi=\mathbf{r}_i;t)&=\sum_j^n[P(\xi=\mathbf{r}_i|\eta=s_j;t)P(\eta=s_j)] \\ &=p_{i.}=\sum_j^n p_{ij}=\sum_j^n p_{i|j}p_{.j}. \end{aligned} \tag{9}$$

Hence, (8) becomes

$$\begin{aligned} P(\eta=s_j|\xi=\mathbf{r}_i;t)&=\frac{P(\xi=\mathbf{r}_i,\eta=s_j;t)}{\sum_j^n[P(\xi=\mathbf{r}_i|\eta=s_j;t)P(\eta=s_j)]} \\ &=\frac{p_{ij}}{\sum_j^n p_{i|j}p_{.j}}=\frac{p_{ij}}{p_{i.}}. \end{aligned} \tag{10}$$

THE CONTINUOUS CASE IN ORDINARY SPACE

Let $f(\mathbf{r}, s; t)$ be the joint frequency function in time for the variables $\mathbf{r}$ and s. Then conditional probabilities may be written for the continuous case in a manner analogous to the discrete systems. We assume that the distribution function $F(\mathbf{r}, s; t)$, which corresponds to the probability function $P(\xi \leqslant \mathbf{r}, \eta \leqslant s; t)$, viz,

$$F(r_1, r_2, r_3, s; t) = P(\xi_1 \leqslant r_1, \xi_2 \leqslant r_2, \xi_3 \leqslant r_3, \eta \leqslant s; t), \tag{11}$$

is everywhere continuous, and that

$$f(r_1, r_2, r_3, s; t) = \frac{\partial^4 F(r_1, r_2, r_3, s; t)}{\partial r_1 \partial r_2 \partial r_3 \partial s} \tag{12}$$

is continuous except for a finite number of curves. Then for any set S, it follows that

$$P(S, t) = \int_S f(\mathbf{r}, s; t) d\mathbf{r} ds, \tag{13}$$

and in particular,

$$\int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty f(r_1, r_2, r_3, s; t) dr_1 dr_2 dr_3 ds = 1. \tag{14}$$

The marginal distribution of ξ will have the probability function

$$P(\xi \leqslant \mathbf{r}; t) = \int_{-\infty}^{r_3} \int_{-\infty}^{r_2} \int_{-\infty}^{r_1} \int_0^\infty f(\mathbf{u}, v; t) dv d\mathbf{u} = \int_{-\infty}^{r_3} \int_{-\infty}^{r_2} \int_{-\infty}^{r_1} f_1(\mathbf{u}; t) d\mathbf{u}, \tag{15}$$

where

$$f_1(\mathbf{r}; t) = \int_0^\infty f(\mathbf{r}, s; t) ds. \tag{16}$$

Similarly, the marginal distribution of η will possess the probability function

$$P(\eta \leqslant s) = \int_0^s \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty f(\mathbf{u}, v; t) d\mathbf{u} dv = \int_0^s f_2(v) dv, \tag{17}$$

where

$$f_2(s) = \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty f(\mathbf{r}, s; t) d\mathbf{r} \tag{18}$$

is precisely the overall particle-size distribution frequency function.

The conditional probability of the event $\xi \leqslant \mathbf{r}$ relative to the hypothesis $s < \eta < s + \Delta s$ is

$$P(\xi \leqslant \mathbf{r} | s < \eta < s + \Delta s; t) = \frac{P(\xi \leqslant \mathbf{r}, s < \eta < s + \Delta s; t)}{P(s < \eta < s + \Delta s)} = \frac{\int_s^{s+\Delta s} \int_{-\infty}^{r_3} \int_{-\infty}^{r_2} \int_{-\infty}^{r_1} f(\mathbf{r}, s; t) d\mathbf{r} ds}{\int_s^{s+\Delta s} \int_{-\infty}^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty f(\mathbf{r}, s; t) d\mathbf{r} ds}. \tag{19}$$

If Δs tends to zero, then

$$\lim_{\Delta s\to 0} P(\xi \leq \mathbf{r}|s<\eta<s+\Delta s;t)=\frac{\int_{-\infty}^{r_3}\int_{-\infty}^{r_2}\int_{-\infty}^{r_1} f(\mathbf{r},s:t)\,d\mathbf{r}}{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f(\mathbf{r},s;t)\,d\mathbf{r}}=\frac{\int_{-\infty}^{r_3}\int_{-\infty}^{r_2}\int_{-\infty}^{r_1} f(\mathbf{r},s;t)\,d\mathbf{r}}{f_2(s)} \tag{20}$$

Eq. (20) is the conditional distribution function in $\mathbf{r}$ for fixed s. If $f(\mathbf{r}, s; t)$ is continuous in $\mathbf{r}$, it may be differentiated with respect to the components of $\mathbf{r}$ to obtain the conditional frequency function

$$f(\mathbf{r}|s;t)=\frac{f(\mathbf{r},s;t)}{f_2(s)}. \tag{21}$$

The probability of the event $\eta \leq s$ on the hypothesis $\mathbf{r}<\xi<\mathbf{r}+\Delta\mathbf{r}$ is

$$P(\eta\leq s|\mathbf{r}<\xi<\mathbf{r}+\Delta\mathbf{r};t)=\frac{P(\eta\leq s,\mathbf{r}<\xi<\mathbf{r}+\Delta\mathbf{r};t)}{P(\mathbf{r}<\xi<\mathbf{r}+\Delta\mathbf{r};t)}=\frac{\int_{r_3}^{r_3+\Delta r_3}\int_{r_2}^{r_2+\Delta r_2}\int_{r_1}^{r_1+\Delta r_1}\int_0^s f(\mathbf{r},s;t)\,ds\,d\mathbf{r}}{\int_{r_3}^{r_3+\Delta r_3}\int_{r_2}^{r_2+\Delta r_2}\int_{r_1}^{r_1+\Delta r_1}\int_0^\infty f(\mathbf{r},s;t)\,ds\,d\mathbf{r}}. \tag{22}$$

If $\Delta\mathbf{r}$ is permitted to approach zero, (22) will yield

$$\lim_{\Delta r\to 0} P(\eta\leq s|\mathbf{r}<\xi<\mathbf{r}+\Delta\mathbf{r};t)=\frac{\int_0^s f(\mathbf{r},s;t)\,ds}{\int_0^\infty f(\mathbf{r},s;t)\,ds}=\frac{\int_0^s f(\mathbf{r},s;t)\,ds}{f_1(\mathbf{r};t)}, \tag{23}$$

which is the conditional distribution function in s for fixed $\mathbf{r}$. If $f(\mathbf{r}, s; t)$ is continuous in s, it may be differentiated with respect to s to determine the conditional frequency function

$$\begin{aligned} f(s|\mathbf{r};t)&=\frac{f(\mathbf{r},s;t)}{f_1(\mathbf{r};t)} \\ &=\frac{f(\mathbf{r}|s;t)f_2(s)}{\int_0^\infty f(\mathbf{r}|s;t)f_2(s)\,ds}. \end{aligned} \tag{24}$$

Eq. (24) is an expression for the frequency function of the particle-size distribution at point $\mathbf{r}$ at time t, and is analogous to (10) for the discrete case.

AN EXAMPLE OF DETERMINATION OF THE JOINT FREQUENCY FUNCTION

Chandrasekhar [4] considers a one-dimensional problem on the effect of gravity on Brownian motion. We will consider this problem further in the light of the foregoing developments by indicating the determination of the joint frequency function. We remark that so far the formalism has not been specifically limited to Brownian motion.

Chandrasekhar applies the Smoluchowski equation,

$$\frac{\partial w}{\partial t}=\nabla\cdot(q\beta^{-2}\nabla w-\mathbf{K}\beta^{-1}w), \tag{25}$$

[4] S. Chandrasekhar, Revs. Modern Phys., 15: 57–9. 1943.

where w is the position frequency function for $t \gg \beta^{-1}$, and

$$q = \beta kT \tag{26}$$

with

$$\beta = \frac{6\pi s\zeta}{m}. \tag{27}$$

In (26) and (27) k is Boltzmann's constant, T, is the absolute temperature, ζ is the coefficient of viscosity of the surrounding medium, and s and m are the characteristic radius and mass of the particle. Stokes' law viscous dissipation is assumed. The vector **K** represents the acceleration caused by an external force field. The semi-infinite region $z > 0$ in a still medium is treated, with the positive z-axis in the vertical direction and gravity as the external field, so that

$$K_x = 0;\ K_y = 0;\ K_z = -[1 - (\rho_0/\rho)]g, \tag{28}$$

where ρ and $\rho_0 (\leq \rho)$ are the densities of the particle and surrounding medium, respectively, and g is the acceleration due to gravity. In this situation, (25) becomes

$$\frac{\partial w}{\partial t} = \frac{q}{\beta^2} \nabla^2 w + \left(1 - \frac{\rho_0}{\rho}\right) \frac{g}{\beta} \frac{\partial w}{\partial z}, \tag{29}$$

which shows that the system may be considered as a diffusion process. Chandrasekhar writes

$$D = \frac{q}{\beta^2} = \frac{kT}{m\beta};\ c = \left(1 - \frac{\rho_0}{\rho}\right) \frac{g}{\beta}, \tag{30}$$

so that (28) takes the form

$$\frac{\partial w}{\partial z} = D \frac{\partial^2 w}{\partial z^2} + c \frac{\partial w}{\partial z}, \tag{31}$$

and then imposes the initial and boundary conditions

$$\lim_{t \to 0} w = \delta(z - z_0); \tag{32}$$

$$D \frac{\partial w}{\partial z} + cw = 0,\ (z = 0,\ t > 0). \tag{33}$$

where $\delta(z - z_0)$ is the Dirac delta function which indicates that all the particles are initially at $z = z_0$. The solution of (31) subiect to the conditions (32) and (33) is

$$w(z,\ t;\ z_0) = \frac{1}{2(\pi Dt)^{1/2}} \left\{ \exp\left[-(z + z_0)^2/4Dt\right] + \exp\left[-(z + z_0)^2/4Dt\right]\right\} \exp\left[-\frac{c}{2D}(z - z_0) - \frac{c^2}{4D} t\right] + \frac{c}{2D} \operatorname{erfc}\left(\frac{z + z_0 - ct}{2(Dt)^{1/2}}\right) \tag{34}$$

Chandrasekhar makes several interesting observations about the physical implications of the solution (34) which we shall not discuss here.[5]

In (34), the constants c and D contain s. Hence, in a system having a particle-size distribution, (34) may be written

$$w(z,\ t;\ z_0) = w(z,\ s,\ t;\ z_0). \tag{35}$$

In applying (34) to a many-particle system, it is presumed that each particle obeys it independently of the other particles. Similarly, we now assume that in the size-distributed system, the particles behave inde-

[5] See pp. 58–59 of footnote 4.

pendently, so that (34) may be considered as the conditional frequency function. Consequently, we now write

$$f(z\,|\,s;\,t)=w(z,\,t;\,z_0). \tag{36}$$

By virtue of (21), the joint frequency function is

$$f(z,\,s;\,t)=w(z,\,t;\,z_0)f_2(s). \tag{37}$$

If, e.g., the particle-size is log-normally distributed, i.e.,

$$f_2(s)=\frac{1}{(2\pi)^{1/2}\,s(ln\sigma)}\exp\left[-\frac{(lns-ln\langle s\rangle)^2}{2(ln\sigma)^2}\right], \tag{38}$$

where $\langle s\rangle$ is the geometric mean particle size and σ is the geometric standard deviation, then combination of (37), (38), and (34) yields

$$f(z,\,s;\,t)=\frac{1}{2\pi(2Dt)^{1/2}\,s(ln\sigma)}\left\{\left[\exp\left[-(z-z_0)^2/4Dt\right]+\exp\left[-(z+z_0)^2/4Dt\right]\right]\exp\left[-\frac{c}{2D}(z-z_0)-\frac{c^2}{4D}t\right]\right.$$
$$\left.+c(\pi t/D)^{1/2}\operatorname{erfc}\left(\frac{z+z_0-ct}{2(Dt)^{1/2}}\right)\right\}\exp\left[-\frac{(lns-ln\langle s\rangle)^2}{2(ln\sigma)^2}\right]. \tag{39}$$

Eq. (39) cannot be written in the form

$$f(z,\,s;\,t)=\phi_1(z,\,t)\phi_2(s,\,t), \tag{40}$$

which points out that z and s are not independent. At least formally, (39) could be used to obtain an expression for $f(s,\,z;\,t)$, the particle-size frequency function for point z at time t.

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